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SCIENTIFIC REPORT NO. 8

HIGH TEMPERATURE SEMICONDUCTOR RESEARCH

CONTRACT NO. AF19(604)-6152

ELECTRONICS RESEARCH DIRECTORATE

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

OFFICE OF AEROSPACE RESEARCH

UNITED STATES AIR FORCE

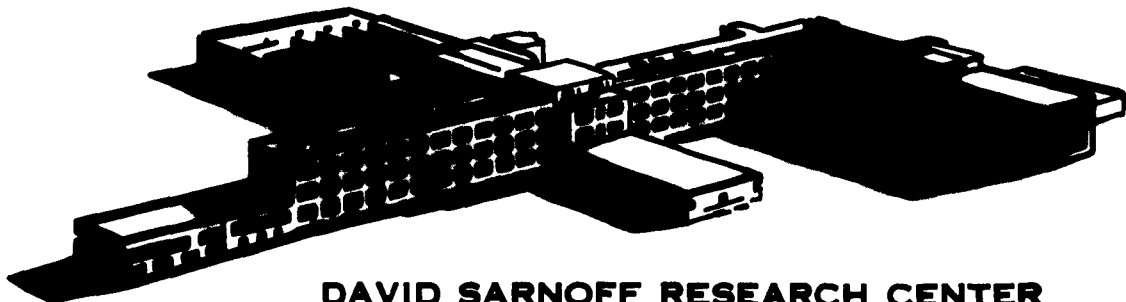
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HIGH TEMPERATURE SEMICONDUCTOR RESEARCH

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RADIO CORPORATION OF AMERICA
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ABSTRACT

The explosions in the high pressure magnetic Czochralski apparatus for the growth of GaP have been mainly eliminated. In repeated tests, boules of GaP have been prepared in this apparatus without difficulty.

Thermally stimulated current measurements of high resistivity GaAs after annealing at 700°C in molten KCN for 16 hours have verified that the concentration of traps in GaAs prepared by the horizontal Bridgman technique are distinctly lower than in GaAs prepared by the floating zone technique. It was further found that the rate of cooling of GaAs crystals subsequent to growth has a marked effect on their electrical properties. Rapidly cooled crystals tend to be high resistivity.

Because of wide discrepancies in measurements reported in the literature, accurate measurements of the temperature variation of the dissociation pressure are being carried out using a quartz Bourdon gauge. This will serve to check the melting point of GaAs and the dissociation pressure at the melting point, since previous determinations of both of these may be in error.

Experiments have been carried out indicating that carbon can be transported during the sublimation of arsenic by both mechanical and chemical means. This, together with other evidence, makes it plausible that the black deposit observed remaining behind after multiple sublimations of spectrographically pure arsenic is carbon. Such carbon is present in concentrations of the order of 10 ppm atomic, and is therefore one of the main impurities in the spectrographically pure arsenic.

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I. GALLIUM PHOSPHIDE CRYSTAL GROWTH*

A major improvement has been accomplished in the High Pressure Magnetic Czochralski Growth Apparatus, namely the explosion hazard has mainly been eliminated. This was made possible by redesigning the ampoule such that the storage reservoir for the excess phosphorus is now located in its top section. As illustrated in Fig. I-1, a quartz insert has been installed to prevent the molten phosphorus from dripping down into the hot crucible. The large separation between the reservoir and the crucible, and the additional shielding from the seed holder, make it now possible to control the temperature of the excess phosphorus reservoir completely independently of the melt temperature. Also, all the thermocouples in the autoclave are now shielded to exclude interference from the R.F. heating coil. In this quarter, no explosions have been encountered after these measures were taken.

With the improved temperature and pressure control, it is now possible to synthesize large quantities of gallium phosphide from the elements. The GaP ingots which were solidified from a stoichiometric melt under 25 atm. of phosphorus pressure are polycrystalline and relatively free of inclusions. In one experiment, a seed was dipped into and slowly withdrawn from the melt, but the pulled material was highly polycrystalline.

*Research in this section performed mainly by W. K. Liebmann.

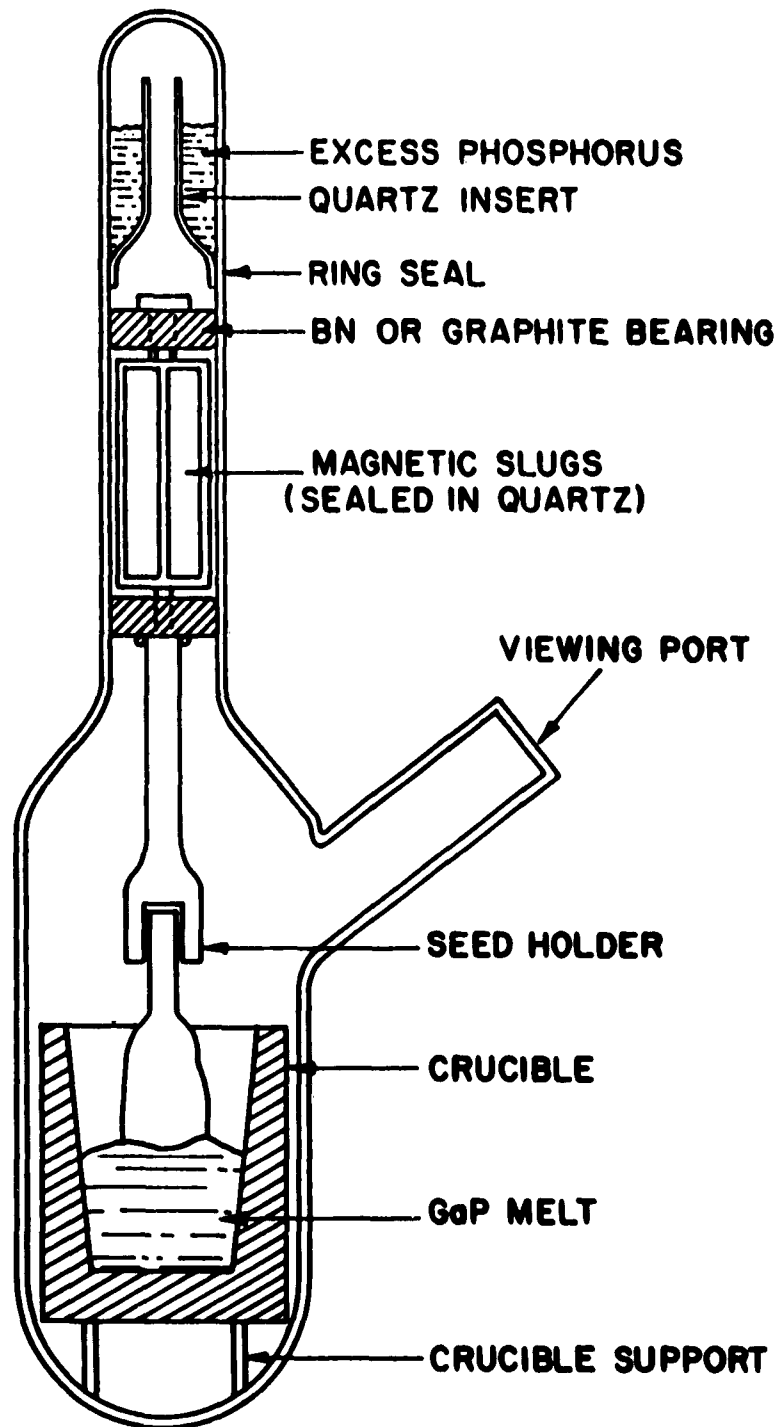


Fig. I-1. Schematic Drawing of Quartz Growth Ampoule for GaP Showing Liquid Phosphorus Reservoir.

II. BEHAVIOR OF DEFECTS IN GaAs

II-A. THERMAL TREATMENT OF GaAs*

Annealing studies in high resistivity GaAs have been continued on material produced both by the horizontal Bridgman method and by floating zone refining. In addition, a program of observing the effects of rapidly quenching ingots after growth has been initiated.

1. ANNEALING AT 700°C IN KCN

In order to further verify the differences in annealing behavior noted in the previous Scientific Report between the horizontal Bridgman high resistivity GaAs and high resistivity GaAs produced by floating zone methods, a sample of RCA material (81-2A) was annealed in KCN simultaneously with a sample of SERL (FZP-2) GaAs in a single quartz ampoule for 16 hours at 700°C, and then quenched. The trap densities in the two samples before and after this anneal are shown in Table II-1, where E and n are the energies and densities of the traps.

TABLE II-1
TRAP DENSITIES IN IDENTICALLY ANNEALED SAMPLES OF HIGH RESISTIVITY GaAs
PRODUCED BY BRIDGMAN AND FLOATING ZONE METHODS

| | $E_1(\text{ev})$ | $n_1(\text{cm}^{-3})$ | $E_2(\text{ev})$ | $n_2(\text{cm}^{-3})$ | $E_3(\text{ev})$ | $n_3(\text{cm}^{-3})$ |
|--------------------|------------------|-----------------------|------------------|-----------------------|------------------|-----------------------|
| Crystal SERL FZP-2 | | | | | | |
| Before Annealing | 0.67 | 4×10^{15} | 0.56 | 4×10^{15} | 0.27 | 5×10^{13} |
| After Annealing | 0.67 | 2×10^{16} | 0.53 | 10^{17} | 0.18 | 8×10^{17} |
| Crystal RCA 81-2A | | | | | | |
| Before Annealing | — | — | 0.53 | 10^{17} | 0.36 | 3×10^{16} |
| After Annealing | — | — | 0.57 | 2×10^{16} | 0.34 | 2×10^{15} |

This experiment demonstrates quite convincingly the trends indicated in the previous Scientific Report: the horizontally grown 81-2A sample has a trap density which is higher than the floating zone FZP-2 before treatments. After annealing in KCN the situation is

*Research in this section performed mainly by J. Blanc, R. H. Bube and L. R. Weisberg.

reversed, with FZP-2 having an increased density of traps, especially of the E_2 and E_3 levels; FZP-2 in fact after annealing has a much higher trap density than 81-2A, whose trap densities *decreased* under annealing.

2. EFFECTS OF GROWTH CONDITIONS

This systematic difference between floating zone refined material and that grown by the horizontal Bridgman method might be due to differences in the growth procedures. In the former case, the crystal is cooled very quickly after solidification to a temperature of around 600°C, while in the latter case the crystal is usually maintained, after solidification, at temperatures of 1000°C or higher for several hours. To see if such growth conditions can, indeed, affect the properties of crystals, a series of horizontal Bridgman grown ingots were quenched immediately after completion of growth by pulling the quartz ampoules out of the furnace and exposing the ampoules to air at room temperature. The ingots quenched in this fashion cool to below 1000°C in 15 minutes. Results for 11 ingots grown in Spectrosil boats, 5 normally cooled and 6 quenched, are shown in Table II-2, where n is the electron density and "high ρ " indicates a resistivity $\geq 10^6$ ohm-cm.

TABLE II-2
EFFECT OF QUENCHING GaAs CRYSTALS GROWN IN SPECTROSIL BOATS
DIRECTLY SUBSEQUENT TO GROWTH

| NOT QUENCHED | | QUENCHED | |
|--------------|----------------------|-------------|----------------------|
| CRYSTAL NO. | $n(\text{cm}^{-3})$ | CRYSTAL NO. | $n(\text{cm}^{-3})$ |
| 84 | 1.4×10^{16} | 81 | High ρ |
| 87 | 2.9×10^{16} | 82 | High ρ |
| 88 | 2.0×10^{15} | 83 | 1.6×10^{16} |
| 89 | 1.4×10^{16} | 85 | High ρ |
| 90 | 2.4×10^{16} | 86 | 1.4×10^{13} |
| | | 93 | High ρ |

Inspection of Table II-2 shows that none of the "normally cooled" ingots were high resistivity and only one had a carrier density lower than 10^{16} cm^{-3} . In contrast, the quenched ingots had quite different characteristics, with only one ingot having an electron density higher than 10^{16} cm^{-3} , four being high resistivity and one being intermediate with a carrier density of $1.4 \times 10^{13} \text{ cm}^{-3}$. These data indicate that the presence of the defects responsible for the high resistivity behavior is markedly dependent on the annealing treatments which GaAs crystals receive immediately subsequent to growth.

II-B. SUMMARY OF PAST ANNEALING RESULTS

A mass of data has been assembled in past Scientific Reports dealing with the annealing behavior of high resistivity GaAs. As an aid in establishing a coherent model for the annealing effects, a summary of previous data which appear to bear on this question is presented below. A satisfactory model should be able to explain the bulk of these data with a minimum of arbitrary assumptions. In what follows, the three traps referred to as the E_1 , E_2 , and E_3 levels previously will be designated by their energies: 0.69, 0.55 and 0.24 ev. These energies are averages for these traps in many different samples and under many treatments; the average deviations from the means are a few hundredths of an electron volt in each case, but the systematic errors inherent in the thermally stimulated current method may be higher. The bulk of the anneals referred to were for a period of 16 hours.

1. TRAP DENSITIES IN AS-GROWN HIGH RESISTIVITY GaAs

- a) In the initial series of measurements by Bube¹ on Bridgman material produced in 1959 and before, densities of the 0.24 and 0.55 ev levels were larger than $6 \times 10^{16} \text{ cm}^{-3}$, with most samples having trap densities larger than 10^{17} cm^{-3} , and up to $2 \times 10^{18} \text{ cm}^{-3}$.
- b) In the current series of measurements on GaAs produced by the Bridgman method in 1961, densities of the 0.24 ev and 0.55 ev levels are generally in the low 10^{16} cm^{-3} range, with about the same density of the 0.69 ev trap. The total trap densities have been as low as 10^{15} cm^{-3} and as high as 10^{17} cm^{-3} .
- c) Floating zone GaAs (both from BTL and SERL) show very low trap densities, namely in the 10^{15} cm^{-3} range or less. Also, the conductivity slopes on these samples above 300°K are larger than 0.8 ev.

2. TRAP DENSITIES IN ANNEALED GaAs

- a) In high resistivity GaAs made by diffusion of copper into low resistivity n-type GaAs in the range 500°-750°C², there is a striking apparent absence of the 0.24 ev level. Evidence for the 0.55 ev and 0.69 ev levels is statistically scant, but these densities where available are in the range 10^{16} - 10^{18} cm^{-3} . The introduction of a sensitizing center for photoconductivity which is a deep acceptor in some way associated with copper should also be noted.
- b) RCA Bridgman high resistivity GaAs exhibits the following set of annealing behavior: annealing in KCN at 700°C gives low trap densities regardless of previous treatment.

¹R. H. Bube, J. Appl. Phys. 31, 315 (1960).

²J. Blanc, R. H. Bube, and H. E. MacDonald, J. Appl. Phys. 32, 1666 (1961).

Annealing in the presence of copper at 500°C introduces of the order of 10^{17} - 10^{18} traps cm^{-3} at both 0.55 eV and 0.24 eV, without changing the density of the 0.69 eV level. Annealing at 700°C in a radiant heat furnace in the absence of KCN after a copper treatment retains the high trap density; subsequent KCN treatment removes the traps. Reheating with copper at 500°C, after trap introduction at 500° and trap removal at 700°C in KCN, returns the trap densities essentially to the values obtained after the first treatment at 500°C. For one sample, there is evidence that heating with copper leads to no appreciable trap introduction below 500°C. For another sample, which was high resistivity p-type, annealing in KCN at 800°C turned the sample low resistivity n-type and this sample could not be returned to a high resistivity state. This change to low resistivity could not be reproduced on a Czochralski grown crystal with very similar initial properties.

c) Floating zone material shows the following annealing behavior: annealing with copper at 500°C turns the material inhomogeneous p-type. Annealing with copper at 450°C introduces between 10^{18} (BTL) and 10^{17} (SERL) traps cm^{-3} at 0.24 eV and 0.55 eV. Annealing in KCN at 700°C increases the trap densities further, up to 10^{20} cm^{-3} for the 0.24 eV trap in BTL sample. Annealing in KCN at 800°C of SERL sample in KCN at 800°C increases trap densities to a total of $\sim 3 \times 10^{18} \text{ cm}^{-3}$. Annealing in KCN at 700°C without copper pretreatment yields essentially the same increase in trap density as with copper pretreatment. In all these treatments, and unlike RCA GaAs, the 0.69 eV trap density also increases, to a maximum in the range of 10^{16} cm^{-3} . The conductivity slopes also no longer exhibit values larger than half the band gap.

3. DONOR DENSITIES IN LOW RESISTIVITY p-TYPE GaAs

a) If low resistivity p-type GaAs is made by diffusing copper into high resistivity GaAs, the total compensating donor concentration is small ($< 10^{16} \text{ cm}^{-3}$)³.

b) If low resistivity p-type GaAs is made by diffusing copper into low resistivity GaAs, there is usually a concentration of compensating donors approximately equal to the shallow donor concentration.

II-C. TEMPERATURES VARIATION OF THE DISSOCIATION PRESSURE OF GaAs*

Accurate values of the temperature variation of the dissociation pressure of GaAs have never been established. Previous investigations⁴⁻⁷ show wide discrepancies in the

³F. D. Rosi, D. Meyerhofer, and R. V. Jensen, J. Appl. Phys. 31, 1507 (1961).

*Research in this section performed mainly by D. Richman.

dissociation pressure measurements, which in turn casts doubt on the measurements of the dissociation pressure at the stoichiometric melting point, and even on the value of the melting point itself. To properly carry out any annealing or even diffusion studies, it can be important to know the dissociation pressures quite precisely. Furthermore, measurements of the temperature variation of the dissociation pressure provides a very sensitive method for determining the melting point of GaAs because of the rapid change of dissociation pressure in the neighborhood of the melting point. Finally, such measurements can disclose a sudden rise in the liquidus of the GaAs phase diagram in the neighborhood of stoichiometry, similar to that found in the phase diagrams of materials such as CdTe and the lead salts.

Three different experimental techniques have been used in past investigations of dissociation pressures: mass spectrometry⁵, dew point measurements^{6,7}, and measurement of the freezing point under an arsenic pressure known by the temperature of an arsenic reservoir⁴. Each of these requires a certain amount of interpretation to derive the arsenic pressure in equilibrium with the GaAs, and furthermore, kinetics of reactions can introduce severe errors in the results. In contrast, measurement of the dissociation pressure by means of a quartz Bourdon gauge seemed desirable since it provides a *direct* measurement of the *equilibrium* pressure, and is capable of uniform sensitivity over the pressure range of 10^{-1} mm to 10^3 mm. A gauge reproducibly readable to ± 0.1 mm was constructed and calibrated against a universal vacuum gauge (McCleod gauge) and a mercury manometer. The procedure and furnaces used were described in the previous Scientific Report. The temperatures and pressures involved in this experiment are sufficiently low so that it was not necessary to encapsulate the sample tube in a graphite block. The temperature of the sample was determined by four thermocouples placed in dimples in the sample tube which were in contact with the solid GaAs. Due to the geometry and sensitivity of the gauge, resonant oscillations were encountered at pressures above 420 mm Hg. Therefore it was not possible to reach the melting point with this gauge. A second gauge of different size and slightly lower sensitivity has been constructed, but measurements with this gauge have not been carried out yet. The results given here are thus not complete and must be considered of a preliminary nature. Points were determined on both heating and cooling. The thermocouples have not yet been calibrated but this shall be done after the pressure measurements are complete.

Figure II-1 shows the points obtained to date along with curves showing the results of the previous investigations. Comments on these results will be reserved until completion

⁴J. van den Boomgaard and K. Schol, Phillips Research Reports 12, 127 (1957).

⁵R. Goldfinger and J. von Drowart, J. Chim. Phys. 55, 721 (1958).

⁶J. W. Laksanen, Unpublished Work.

⁷V. J. Lyons and V. J. Silvestri, J. Phys. Chem. 65, 1275 (1961).

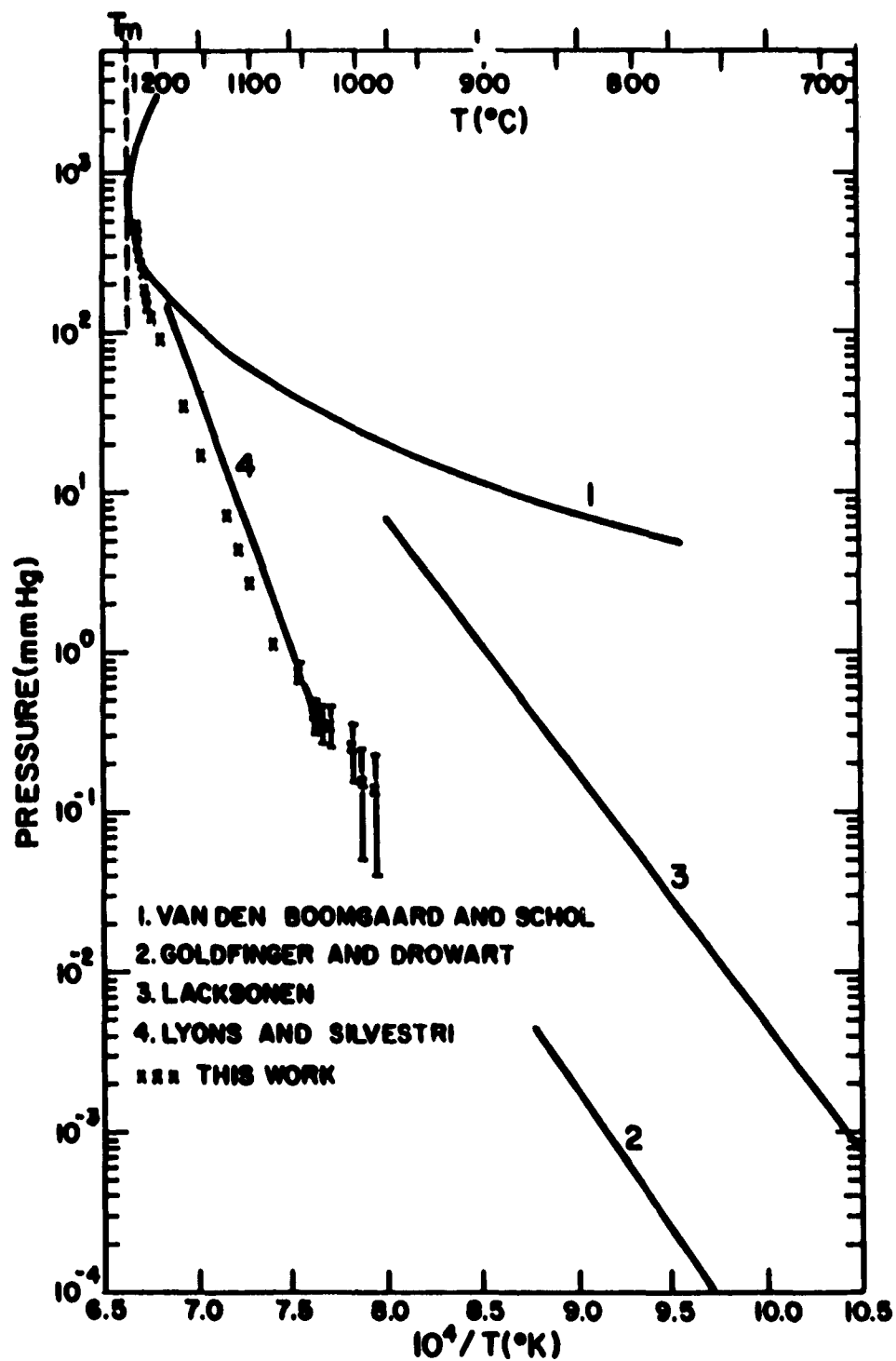


Fig. II-1. Temperature Variation of Dissociation Pressure of GaAs

of this work but it should be pointed out that, as seen in Fig. II-1, the dissociation pressure at the melting point is not well established. Extrapolation of any of the low temperature results to the reported melting point, taking into account the expected curvature of the $\log P$ vs. $1/T$ plot indicate that the dissociation pressure of GaAs may be somewhat higher than that reported by van den Boomgaard and Schol.⁴ This latter data is especially suspect since it is quite inaccurate at temperatures well below the melting point.

III. CARBON IN ARSENIC: EVIDENCE FOR ITS EXISTENCE AND TRANSPORT*

III-A. INTRODUCTION

Arsenic is presently available commercially in a state of purity exceeding 99.999% as determined by emission spectrography. Such arsenic is used commonly in the preparation of high purity semiconductors such as GaAs and InAs. One element that is not spectrographically detectable is carbon, and further there are no simple methods available for detecting the presence of carbon in concentrations below 25 atomic ppm. However, as described later, carbon is suspected to be one of the main residual impurities in arsenic, and to be present even after arsenic is multiply sublimed. The purpose of this section is to describe evidence for the existence of carbon in arsenic, and for its transport during sublimation of the arsenic.

III-B. RESULTS

A black deposit is observed to remain behind after arsenic is slowly sublimed. When this black deposit is heated, a large fraction of the deposit can be observed to glow red and yet not sublime, suggestive of carbon. In addition, when heated in air, the deposit disappears from view. Such a deposit will continue to appear, even after the arsenic is resublimed two or three times. The amount of residue depends upon the rate of sublimation, the temperature gradient, and the geometry of the vessel. To determine the concentration of the black deposit, roughly 12 g of triply sublimed arsenic** was placed at one end of a 14 mm bore quartz tube that was subsequently sealed under a vacuum of 10^{-6} torr. The tube was placed in a horizontal furnace with the end of the tube containing the arsenic held at 420°C, and the other end at room temperature, so that the arsenic sublimed along the tube and left a black deposit. After breaking open the quartz tube, the deposit was removed with a small piece of paper and weighed on a microbalance. The results of three such tests indicated that the black deposit weighed of the order of 10^{-5} g. If the deposit were carbon, this would represent a minimum of 3 atomic ppm in the arsenic originally, since more can be removed on subsequent sublimations. Using arsenic from other sources, considerably greater deposits were observed. In this latter case, carbon is especially implicated since

* Research in this section performed mainly by L. R. Weisberg and J. Blanc.

**Purchased from the American Smelting and Refining Co. (ASARCO).

few other non-volatile impurities are present in the arsenic. However, if it is concluded that the black residue is, indeed, carbon, the question still remains of why the carbon is not removed to a fuller extent by the sublimation of the arsenic.

Three possibilities were investigated as possible methods of transport of the carbon during the sublimation of arsenic: the existence of carbon in the form of volatile hydrocarbons, mechanical transport*, or chemical reaction between the arsenic and carbon. The first of these was of interest because it has previously been observed that one of the major impurities in multiply distilled phosphorus is carbon, and it apparently exists in the form of a hydrocarbon, since the carbon can be removed from the phosphorus by passing the phosphorus vapor through a quartz tube held at 1100°C.¹

This same procedure was attempted for arsenic. A three temperature zone horizontal furnace was used, and the arsenic was sublimed in an evacuated sealed quartz ampoule from the first zone to the third zone through a center "cracking" zone. The center section of the ampoule in some tests was filled with quartz chips to greatly increase the available surface area. Although a wide variety of temperature conditions were investigated, including cracking zone temperatures between 500° and 1200°C, at no time were any black deposits seen in any place except the first zone as usual. It can be concluded that carbon is not present in the arsenic in the form of volatile hydrocarbons that readily decompose at temperatures below 1200°C.

The next possibility tested was that of mechanical transport. Several tests were carried out in which both finely powdered graphite and 10 g of arsenic were added to the bottom of a 14 mm bore, 32 cm long, quartz tube. The arsenic oxide was removed by vacuum heating at 350°C, and subsequently the tube was sealed under vacuum. The tube was lowered vertically into a furnace held at 500°C at a rate of 1 cm per hour. After 3/4 of the tube was lowered into the furnace, all of the arsenic had sublimed to the top, and no carbon was visible at the bottom of the tube! As much as 2 mg of carbon could be transported in this fashion, however when 5 mg of carbon was used, some powdered carbon still remained at the bottom, and was not transported in several subsequent sublimations. This indicates that there is an upper limit to the amount of carbon that can be transported for a given geometry, temperature gradient, and rate of travel.

Two experiments were performed to show that this transport of carbon occurred mechanically rather than chemically. First, the carbon was recovered by simply subliming the arsenic in the tube with the tube held horizontally. Second, attempts were carried out

*i.e., transport of the carbon due to collisions with arsenic atoms, analogous to transport in a diffusion pump.

¹R. J. Guire, Unpublished Work.

to transport the carbon in a horizontal tube in which the carbon was contained in the bottom of a small quartz boat located inside the tube. The arsenic was sublimed from one end of the tube to the other by either slowly moving the tube into the furnace, or else slowly raising the furnace temperature with the tube stationary. In some tests, the arsenic was first sublimed into the boat and then sublimed out again. Even when as little as 1.7 mg of carbon powder was used, no transport of the powder could be discerned. However, when the tube was turned over so that the carbon fell out of the boat to alongside the boat, the carbon was transported on the subsequent sublimation of the arsenic. This strongly suggests that the transport of carbon in the vertical tube was mechanical in nature, and was probably enhanced by the convection currents of arsenic vapor in the tube. In the horizontal tests, the boat interrupted the flow of arsenic atoms.

The possibility of chemical transport of carbon was examined with the use of radioactive C^{14} . A piece of quartz was coated with a very adherent radioactive carbon film by cracking acetone having an activity of 2.6 mc/millimole. Such a carbon film cannot be removed from the quartz even by rubbing vigorously with paper. This coated piece of quartz was placed at the bottom of a 14 mm bore quartz tube with 10 g of arsenic. Again, the arsenic oxide was removed and the tube sealed under vacuum. The tube was lowered vertically at 1 cm per hour into the furnace held at 500°C . Several samples of arsenic were removed after fracturing the tube, and their radioactivity was counted in a flow counter having a 74% counting efficiency for beta particles. It can be shown that the density of disintegrations per second per cm^3 is given by $4ab$, where $a = 1480 \text{ cm}^{-1}$ for C^{14} , and b is the number of emergent beta particles per second per cm^2 . Provided the surface area is known, the density of carbon atoms in the arsenic can be easily computed. Assuming that the surface area was effectively smooth (beta particles emerging from cracks in the surface would probably not be counted), the number of carbon atoms per cm^3 in the sublimed arsenic was found in all cases to equal 1.3×10^{16} within an experimental error of a factor of 50% in the estimate of the surface area. The uniformity of the carbon distribution is evidence that the carbon was not in the form of individual particles of appreciable size, and further the carbon film on the quartz did not appear to have flaked off in any place. This implies that the carbon was not transported mechanically in this case. It can therefore be concluded that small (0.1 to 1 atomic ppm) quantities of carbon can be transported due to chemical reaction with the arsenic. The chemical species of the carbon-arsenic compound is not known. However, residual quantities of hydrocarbons or water vapor due to degassing of the quartz might lead to the formation of a volatile metal-organic compound. Alternatively, the existence of a compound As_2C_6 has been reported.²

²E. de Mahler, Bull. Soc. Chim. 29, 1072 (1921).

An observation is recorded here in passing. After subliming metallic arsenic in a vacuum, at least three different additional allotropic forms are observed. The first to deposit is a yellow-brown form that is unstable and rapidly converts into the second shiny black form. This black form has a vapor pressure much higher than that of metallic arsenic, and when heated, is observed to sublime almost explosively, spewing pieces of arsenic along the tube. The third form is dull gray in color, resembling a cigar ash, and is the last of the arsenic to sublime. This species appears to have a vapor pressure about an order of magnitude below that of metallic arsenic. The large difference in the vapor pressures between these species of arsenic necessitates special attention in sublimation experiments.

III-C. CONCLUSIONS

Carbon can be transported during the sublimation of arsenic by mainly mechanical, but also in part chemical, means. Therefore, sublimation of arsenic is not a highly efficient means of removing carbon. This fact, together with the observation of a very low vapor pressure black deposit remaining after the sublimation of arsenic, indicates that carbon is one of the main residual impurities in spectrographically pure arsenic, and is present in quantities of the order of 10 atomic ppm. The transport results further imply that the use of carbon in ampoules employed for the growth of GaAs or InAs should be avoided.